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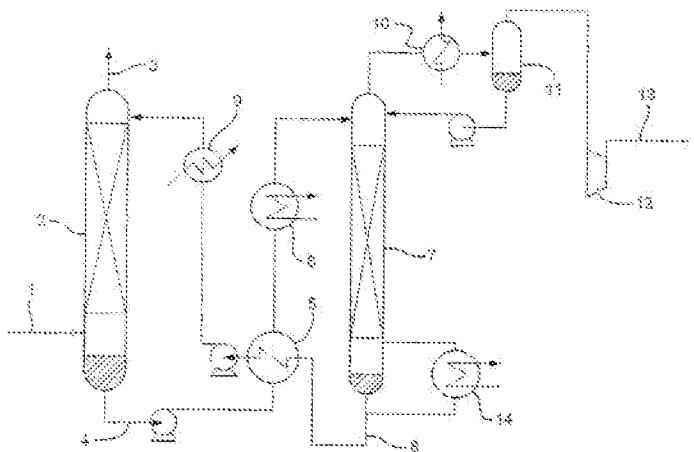
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(54) Title: PROCESS FOR REMOVAL OF ACID GASES

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- (57) Abstract: A process for the removal of an acid gas from a gaseous feed stream comprising contacting the gaseous feed stream with an absorbing fluid to produce (a) a refined gaseous stream having a reduced acid gas content and (b) an acid gas rich absorbing fluid, wherein the absorbing fluid comprises an aqueous solution of a tertiary alkylamine having a concentration of tertiary alkylamine of above 60% by weight, and the tertiary alkylamine is selected from the group consisting of: diamines of formula: (I) $(R^1)_2N(CR^2R^3)_2N(R^1)_2$; triamines of formula: (II) $(R^1)_2N(CR^2R^3)_2N(R^1)(CR^2R^3)_2N(R^1)_2$ and tetramines of formula: (III) $(R^1)_2N(CR^2R^3)_2N(R^1)(CR^2R^3)_2N(R^1)_2N(R^1)_2$, where each R is independently a substituted or unsubstituted C₁ - C₄ alkyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl or, alternatively, the two R¹ groups together with the nitrogen atom

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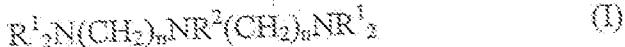
PROCESS FOR REMOVAL OF ACID GASES

The present invention relates to a process for the removal of acid gases, in particular, highly concentrated carbon dioxide (CO_2) and/or hydrogen sulfide (H_2S) from a gaseous stream, comprising an absorption step of bringing the gaseous stream into gas-liquid contact with an absorbing fluid comprising an aqueous solution comprising at least one selected tertiary alkylamine.

US 5,853,680 relates to a process for the removal of highly concentrated CO_2 from high-pressure natural gas to produce refined natural gas, whereby the separated carbon dioxide can be obtained in a relatively high-pressure state which is beneficial for the purpose of injection when it is utilized in tertiary oil recovery or stored permanently in a subsurface structure. It is said that, by employing a specific process using, among various absorbing fluids having the ability to absorb CO_2 , an absorbing fluid having so-called physical absorbing power characterized by the marked temperature dependence of saturated CO_2 absorption level, CO_2 having a much higher pressure than that obtained by conventional processes can be separated at low energy cost with much more simplified equipment than used in conventional systems. In particular, US 5,853,680 is concerned with a process for the removal of highly concentrated CO_2 from high-pressure natural gas which comprises an absorption step of bringing high-pressure natural gas having a CO_2 partial pressure of 2 kg/cm^2 or greater and a pressure of 30 kg/cm^2 or greater (the term "pressure" meaning an absolute pressure) into gas-liquid contact with a regenerated CO_2 -lean absorbing fluid comprising a CO_2 absorbing fluid of which the difference in saturated CO_2 absorption level between 40°C and 120°C is not less than 30 Nm^3 per ton of solvent at a CO_2 partial pressure of 2 kg/cm^2 , whereby highly concentrated CO_2 present in the high-pressure natural gas is absorbed into the

CO₂-lean absorbing fluid to produce refined natural gas having a reduced CO₂ content and a CO₂-rich absorbing fluid; and a regeneration step of heating the CO₂-rich absorbing fluid without depressurizing it, whereby high-pressure CO₂ having a pressure of 10 kg/cm² or greater is liberated and a CO₂-lean absorbing fluid is regenerated and recycled for use in the absorption step. Examples of suitable absorbing fluids for use in the process of US 5,853,680 include an aqueous solution of N-methyldiethanolamine (MDEA), an aqueous solution of triethanolamine, and an aqueous solution of potassium carbonate, as well as these solutions having a CO₂ absorption promoter (e.g. piperazine) added thereto.

US 6,267,939 relates to the use of aqueous solutions of polyalkylene polyamines for the purification of gases containing acidic components primarily for rendering natural gas free of carbon dioxide. The polyalkylene polyamines are of the general formula



wherein

n is 2 or 3,

the R³ groups represent methyl or one of them is hydrogen and the others are methyl, and

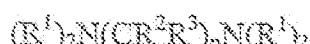
R² is hydrogen, methyl or a group of the formula -(CH₂)₂₋₃-N(CH₃)₂. It is stated that the composition according to the invention comprises one or more polyamine(s) of formula (I) as an aqueous solution of 20-60% by weight, preferably 30-50% by weight. US 6,257,939 is silent concerning regeneration of the carbon dioxide rich aqueous solution of the polyamine(s) of formula (I).

It has now been found that an acid gas may be removed from a gaseous feed stream by employing an absorbing fluid comprising an aqueous solution of at least one selected tertiary alkylamine. These selected tertiary alkylamines have a high absorbance capacity for an acid gas and may be employed at high concentrations, for example, at concentrations of above 60% by weight. Furthermore, acid gas-rich solutions of these selected tertiary alkylamines may be regenerated at above atmospheric pressure, preferably at pressure of above 3 kg/cm² (absolute) and of less than 10 kg/cm² (absolute).

Thus, according to the present invention there is provided a process for the removal of an acid gas from a gaseous feed stream comprising:

(A) an absorption step of bringing the gaseous feed stream into gas-liquid contact with an absorbing fluid, whereby at least a portion of the acid gas present in the gaseous feed stream is absorbed into the absorbing fluid to produce (a) a refined gaseous stream having a reduced acid gas content and (b) an acid gas rich absorbing fluid, characterized in that the absorbing fluid comprises an aqueous solution of at least one tertiary alkylamine selected from the group consisting of:

5 diamines of formula I



I

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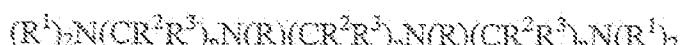
triamines of formula II



II

15

and tetramines of formula III



III

where each R is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably 20 methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ 25 groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4; however, it is preferred that R² and R³ are each hydrogen and n is an integer from 2 to 4, preferably 2; and

(B) a regeneration step of heating the acid gas rich absorbing fluid at a pressure greater than atmospheric pressure whereby a gaseous stream comprising the acid gas is 30 liberated and an acid gas lean absorbing fluid is regenerated and recycled for use in the absorption step.

The gaseous feed stream may be a high-pressure gaseous feed stream, for example, a high-pressure natural gas stream. Alternatively, the gaseous feed stream

may be a low-pressure gaseous feed stream, for example, a combustion gas stream from a power station or refinery. By high-pressure gaseous feed stream is meant a gaseous stream having a pressure of 15 kg/cm² (absolute pressure) or greater and an acid gas content of 1% by volume or greater, preferably of 2 % by volume or greater. By low-pressure gaseous feed stream is meant a gaseous stream having a pressure of at or close to atmospheric pressure and an acid gas content of 1.5 % by volume or greater.

Preferably, the acid gas is selected from the group consisting of carbon dioxide and hydrogen sulphide. Typically, the high-pressure gaseous feed stream or the low-pressure gaseous feed stream contains both carbon dioxide and hydrogen sulphide.

Suitably, the amount of carbon dioxide in the high-pressure gaseous feed stream is in the range 1 to 95% by volume. Typically, an unrefined high-pressure natural gas stream comprises 1 to 40 % by volume carbon dioxide, preferably 5 to 25% by volume, for example, 10 to 15% by volume. Suitably, the amount of hydrogen sulphide in the unrefined high-pressure natural gas stream is at least 0.02% by volume (at least 200 ppmv). Where the refined high-pressure natural gas stream is to be transported through a pipeline, for example, to an electricity generating power station or to a domestic gas distribution system, it is desired to reduce the amount of carbon dioxide in the refined high-pressure natural gas stream to a level of less than 3 % by volume, preferably less than 2% by volume. Suitably, the amount of carbon dioxide in the refined high-pressure natural gas stream may be further reduced using the process of the present invention. For example, where the refined high-pressure natural gas stream is to be employed as a feed stream to a cryogenic processing unit for generating liquefied natural gas (LNG), it is desired to reduce the amount of carbon dioxide in the refined high-pressure natural gas stream to a level of less than 100 ppmv, preferably to a level of 50ppmv or less. In both cases, it is preferred to reduce the amount of hydrogen sulphide in the refined high-pressure natural gas stream to a level of less than 10 ppmv, more preferably 4 ppmv or less.

The amount of carbon dioxide in the low-pressure gaseous feed stream is at least 1.5% by volume. Suitably, the amount of hydrogen sulphide in the low-pressure gaseous feed stream is less than 0.02% by volume (less than 200 ppmv). Preferably, the amount of carbon dioxide in the refined low-pressure gaseous stream is reduced to a value of less than 100 ppmv, more preferably 50ppmv or less. Preferably, the amount of hydrogen sulphide in the refined low-pressure gaseous stream is reduced to a value of

less than 10 ppmv, more preferably 4 ppmv or less.

Preferably, the absorption step is carried out at a temperature of from 20 to 70°C, for example, 30 to 50°C.

Preferably, the high-pressure gaseous feed stream is at a pressure of at least 30 5 kg/cm² (absolute pressure), more preferably at least 40 kg/cm² (absolute pressure), for example, in the range 40 to 70 kg/cm² (absolute pressure).

Preferably, the low-pressure gaseous feed stream is at a pressure of less than 3 kg/cm² (absolute), for example less than 2 kg/cm² (absolute).

The absorbing fluid used in the process of the present invention comprises an 10 aqueous solution of at least one tertiary alkylamine of formula I, II or III (hereinafter "aqueous amine solution"). Suitably, the aqueous amine solution has a tertiary alkylamine concentration of at least 30 % by weight, preferably at least 40 % by weight, more preferably at least 50 % by weight, most preferably greater than 60% by weight. Typically, the aqueous amine solution may have a tertiary alkylamine concentration in 15 the range 30 to 90 % by weight, preferably in the range 62.5 to 90% by weight, more preferably in the range 70 to 80% by weight, for example, 75 % by weight.

Where the aqueous amine solution has a tertiary alkylamine concentration of greater than 60 % by weight, it is envisaged that the acid gas rich absorbing fluid may be heated in the regeneration step at above atmospheric pressure or at atmospheric 20 pressure.

Preferably, the number of moles of basic groups per litre of aqueous amine solution (B) is at least 4, more preferably at least 6, most preferably, at least 7 where B = [1000 x (aqueous amine solution density) x (weight fraction of tertiary alkylamine) x (number of basic groups per molecule of tertiary alkylamine)]/molecular weight of 25 tertiary alkylamine. For example, the number of moles of basic groups per litre (B) for an absorbing fluid comprising a 75% by weight aqueous solution of pentamethyltriethylenetriamine is [1000 x 0.872 x 0.75 x 3]/173.3 = 11.3.

Preferably, the ratio of the molecular weight of the tertiary alkylamine of formula I, II or III to the number of basic functional groups in the tertiary alkylamine is 30 not more than 100:1, more preferably not more than 75:1, most preferably not more than 60:1.

Examples of suitable diamines of formula I include tetramethylethylenediamine, tetraethylethylenediamine, tetramethyl-1,3-propanediamine, tetraethyl-1,3-

propanediamine, tetramethyl-1,3-butanediamine, tetramethyl-1,4-butanediamine, tetraethyl-1,3-butanediamine, tetraethyl-1,4-butanediamine. Examples of suitable triamines of formula II include pentamethyldiethylenetriamine, pentaethylidiethylenetriamine, pentamethyldipropyleneetriamine and pentamethyl-(2-aminoethyl)-1,3-propanetriamine. Examples of suitable tetramines of formula III include hexamethyltriethylenetetramine and hexaethyltriethylentetramine.

Optionally, the aqueous amine solution may comprise a further absorbent selected from the group consisting of N-methyldiethanolamine (MDEA), triethanolamine, and potassium carbonate, preferably MDEA. Suitably, the concentration of the optional further absorbent in the aqueous amine solution is in the range 1 to 40% by weight, preferably 5 to 40% by weight.

It is also envisaged that an absorption promoter (e.g., piperazine) may be added to the aqueous amine solution. Preferably, the concentration of the optional absorption promoter in the aqueous amine solution is in the range 1 to 15 mole %, typically about 5 mole % based on the amount of amine in the aqueous amine solution.

The process of the present invention comprises a regeneration step of heating the acid gas rich absorbing fluid at a pressure greater than atmospheric pressure whereby a gaseous stream comprising the acid gas is liberated and an acid gas lean absorbing fluid is regenerated and recycled for use in the absorption step.

In the regeneration step, the acid gas rich absorbing fluid is preferably heated at a pressure of at least 3 kg/cm² (absolute), more preferably at least 4 kg/cm² (absolute), most preferably at a pressure of at least 6 kg/cm² (absolute), for example, at a pressure of at least 8 kg/cm² (absolute) so as to liberate a relatively high pressure gaseous stream comprising the acid gas therefrom. It is particularly preferred that the acid gas rich absorbing fluid is heated in the regeneration step at a pressure of less than 10 kg/cm² (absolute), for example at a pressure in the range 5 to 9.5 bar (absolute). Where the gaseous feed stream is a low-pressure gaseous feed stream, it is necessary to increase the pressure of the acid gas rich absorbing fluid prior to the regeneration step.

It is preferred that the acid gas rich absorbing fluid is heated in the regeneration step to a temperature of at least 100°C, preferably, to a temperature in the range 150 to 250°C.

An advantage of the absorbing fluid employed in the process of the present invention is that the selected tertiary alkylamines of formula I, II or III can liberate acid

gas easily when heated in the regeneration step, for example, at a relatively high temperature and a relatively high acid gas partial pressure. A further advantage of the absorbing fluid employed in the process of the present invention is that the selected tertiary alkylamines have higher stabilities at the heating temperature of the
5 regeneration step than the amines disclosed in US 5,853,680. Yet a further advantage of the process of the present invention relates to the acid gas loading of the amine. The selected tertiary alkylamine(s) employed in the process of the present invention has a high acid gas loading and hence for a given concentration of acid gas in the gaseous feed stream and for a given feed rate of the gaseous feed stream to the absorption step,
10 the rate at which the absorbing fluid is recycled from the regeneration step to the absorption step will be reduced. For example, in comparison to a process employing an absorbing fluid consisting essentially of an aqueous solution of MDEA, the rate of recycle of the absorbing fluid to the regeneration step may be reduced by up to 45%.

Preferably, the gaseous stream comprising the acid gas that is liberated during
15 the regeneration step is dumped into an underground zone for the purpose of storage. For example, the gaseous stream comprising the acid gas may be injected into a hydrocarbon bearing subterranean formation, in particular, an oil-bearing subterranean formation for the purpose of storage and/or enhanced oil recovery. The liberated gaseous stream will require pressurizing to a pressure that is sufficiently high to permit
20 injection into the underground zone. However, an advantage of carrying out the regeneration step at above atmospheric pressure is that low pressure stages of compression may be eliminated. For example, carrying out the regeneration step at a pressure of 5 kg/cm² (absolute) permits at least one stage of compression to be eliminated while carrying out the regeneration step at a pressure of 9.5 kg/cm² has the
25 potential to eliminate up to 3 stages of compression when compared with liberating the acid gas at atmospheric pressure.

It is also envisaged that the process of the present invention may be used to produce a purified high-pressure carbon dioxide stream for use in enhanced oil recovery by contacting a high-pressure gaseous feed stream having a high carbon dioxide content
30 with the absorbing fluid in the absorption step to generate a carbon dioxide rich absorbing fluid and liberating a purified high-pressure carbon dioxide stream from the carbon-dioxide rich absorbing fluid in the regeneration step. Thus, the gaseous feed stream may comprise a high-pressure gaseous stream having a carbon dioxide content of

20 to 95% by volume, preferably 50 to 95% by volume, for example 80 to 95% by volume. A refined high-pressure carbon dioxide stream having a reduced content of gaseous hydrocarbons is recovered in the regeneration step for use in enhanced oil recovery.

5 It is also envisaged that the process of the present invention may be used to recover carbon dioxide from the gas that is produced from a hydrocarbon-bearing formation during enhanced oil recovery (i.e. during a carbon dioxide flood).

In a further aspect of the present invention there is provided a process for the removal of an acid gas from a gaseous feed stream comprising: (A) an absorption step 10 of bringing the gaseous feed stream into gas-liquid contact with an absorbing fluid, whereby at least a portion of the acid gas present in the gaseous stream is absorbed into the absorbing fluid to produce (a) a refined gaseous stream having a reduced acid gas content and (b) an acid gas rich absorbing fluid, wherein the absorbing fluid comprises an aqueous solution of at least one tertiary alkylamine selected from the group 15 consisting of:

diamines of formula I



20 where each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an 25 integer from 1 to 4, preferably 2 to 4;

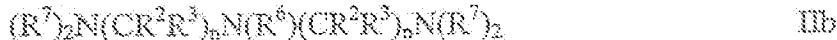
triamines of formula IIa



30 where R⁴ is a substituted or unsubstituted C₂ - C₄ alkyl, preferably ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R⁵ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R⁵ groups together with the nitrogen atom form a

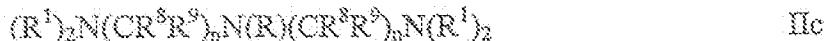
heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4;

5 triamines of formula IIb



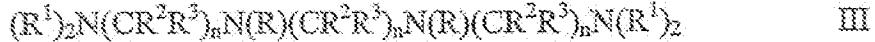
where R⁶ is a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R⁷ is independently a substituted or unsubstituted C₂ - C₄ alkyl selected from ethyl, n-propyl, i-propyl, n-butyl, i-butyl and t-butyl or, alternatively, the two R⁷ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4; and

triamines of formula IIc



where R is a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R⁸ and R⁹ are independently a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR⁸R⁹ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4;

and tetramines of formula III



where each R is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably

methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4; and
5 (B) a regeneration step of heating the acid gas rich absorbing fluid at atmospheric pressure whereby a gaseous stream comprising the acid gas is liberated and an acid gas lean absorbing fluid is regenerated and recycled for use in the absorption step.

10 An exemplary system which can be employed to carry out the process of the present invention is specifically described below with reference to Figure 1

In Figure 1, reference numeral 1 designates natural gas; 2, an absorption tower; 3, refined natural gas; 4, an acid gas rich absorbing fluid; 5, a heat exchanger; 6, a heater; 7, a regeneration tower; 8, an acid gas lean absorbing fluid; 9, a cooler; 10, an overhead condenser; 11, a separating drum; 12, a compressor; 13, high-pressure acid gas; and 14, a reboiler. By way of example, the conditions for removing acid gas from natural gas by employing the system of Figure 1 and using a 75 wt. % aqueous solution of pentamethyldiethylenetriamine (PMDETA) as absorbing fluid are given below.
15 Natural gas 1 having an acid gas content of 12 % by volume, a pressure of 41 kg/cm² and a temperature of 40°C is fed to the lower part of an absorption tower 2. This absorption tower 2 contains either trays or a packing material, for example, an irregular packing material so that the ascending natural gas will come into efficient gas-liquid contact with an acid gas lean absorbing fluid fed to the upper part thereof. The refined natural gas 3 having been freed of acid gas by contact with the acid gas lean absorbing fluid, which now has an acid gas content of 2 % by volume, a temperature of 40°C and a pressure of 41 kg/cm², is discharged from the top of absorption tower 2. On the other hand, the acid gas lean absorbing fluid having absorbed acid gas turns into an acid gas rich absorbing fluid 4, which is transferred to a regeneration stage and regenerated therein.
20

25 The regeneration stage essentially comprises a heat exchanger 5, a heater 6 and a regeneration tower 7. Acid gas rich absorbing fluid 4 is heated in heat exchanger 5 by heat exchange with a hot acid gas lean absorbing fluid 8 which will be described later, further heated with heater 6 using a heat source, for example, steam, and then fed to

regeneration tower 7 that is operated at a pressure of 5 to 6 kg/cm² (absolute). The purpose of regeneration tower 7 is to separate acid gas from the absorbing fluid to produce an acid gas lean absorbing fluid, 8. The regeneration tower is also provided with a reboiler, 14. The liberated acid gas is cooled in overhead condenser 10 and separated from any entrained absorbing fluid in a separating drum 11. This acid gas, which has a relatively high pressure of 5 to 6 kg/cm² (absolute) at a temperature of about 40°C, is compressed to a pressure of 150 kg/cm² by means of a series of compressors 12. An advantage of operating the regeneration stage at a pressure of 5 to 6 kg/cm² (absolute) compared with at atmospheric pressure is that this eliminates low pressure compression demand. The resulting high-pressure acid gas is used for the purpose of tertiary oil recovery or is stored in a suitable sub-surface structure.

On the other hand, the acid gas lean absorbing fluid 8 withdrawn from the bottom of regeneration tower 7, which has a temperature of about 160°C, is cooled in heat exchanger 5 by heating acid gas rich absorbing fluid 4 as described above. The acid gas lean absorbing fluid 8 is then further cooled with a cooler 9 using air, cooling water, seawater or the like, before being recycled to the upper part of absorption tower 2.

The invention will be illustrated with reference to the following Examples.

Apparatus

The apparatus comprised a pressure vessel consisting of a barrel fitted with a manually adjustable piston. The maximum distance through which the piston could travel was 28.5 cm. The internal diameter of the barrel was 5.08 cm giving an internal displaceable volume of 570 cm³. The pressure vessel had a maximum operating pressure of 3000 psia and a potential compression-factor of over 12. The material from which the vessel was constructed was corrosion resistant 316 stainless steel. AFLAS™ and neoprene™ piston seals were employed as these were tolerant to hot hydrogen sulphide, carbon dioxide and amines. Ports were drilled in the end of the barrel for: introducing gas and absorbing fluid; flushing the barrel with water to remove the absorbing fluid; and sampling of the gas phase. Temperature and pressure taps were placed in the ports. All connecting tubing and valves were Swagelok™ 1/16 inch so as to minimize dead volume losses. The vessel was placed in a metal shroud. Beaded heating wire was wrapped around the metal shroud for heating the air bath formed between the vessel and the shroud. The shroud and its heating wire were covered with

a high-temperature insulation material and a tin cover.

Operational sequence

The sequence of operation of the pressure vessel was as followed:

1. Load the barrel of the vessel with an appropriate amount of acid gas and methane (e.g. 54 psia CO₂ and 396 psia CH₄ for a gas mixture comprising 12% by volume CO₂);
2. Inject the appropriate solvent mixture (absorbing fluid);
3. Adjust the temperature to 40°C;
4. Wait for the system to reach equilibrium at the first target pressure (typically 700 psia), and record the piston position (from which the gas volume is calculated);
5. Repeat steps 3 and 4 for pressures of 600, 500, 400, 300, and 200 psia;
6. Heat the vessel to 120°C and repeat steps 4 and 5 at pressures of 700, 600, 500, 400 and 300 psia;
7. Clean the vessel by flushing with water, dry the vessel under vacuum and then load the vessel with the same amount of absorbing fluid and methane, but no acid gas;
8. Set the piston position to each of the values recorded in step 4 above;
9. Record the pressure in the barrel - this is the total partial pressure for the amine, water vapour and methane;
10. Calculate the acid gas partial pressure (i.e. the difference between the pressure in step 9 and the target pressure of Step 4).

Measuring the internal volume of the barrel

The position of the piston was measured to an accuracy of 0.001 cm using electronic calipers. This provided an indication of the internal volume of the barrel. Fine adjustments to the volume were made to account for acid gas absorption and to achieve the target pressure at the target temperature.

Adding a standard amount of absorbing fluid

Once the vessel was filled with gas, an Aldex™ high-pressure (5000 psia) metering pump was used to inject a precise weight of absorbing fluid into the sealed vessel by drawing absorbing fluid from a reservoir that was placed on a balance. A correction was made for the dead volume of the tubing leading from the reservoir to the vessel.

Temperature control

Two temperature controllers were used to maintain the gas at the target

temperature. A control thermocouple was attached to the outer surface of the barrel of the pressure vessel while a recording thermocouple extended into the gas space of the barrel. The internal temperature was controlled to within 0.1°C of the target temperature.

5 Pressure measurement

The pressure was measured using two Merigauge™ digital pressure gauges to an accuracy of 0.1 psia. The pressure gauges accessed the interior of the barrel of the pressure vessel.

Absorption of CO₂:

10 The results presented in Table 1 were obtained using a gaseous stream comprising 12% by volume CO₂ and 88% by volume methane. CO₂ absorption was measured at a temperature of 40°C and a partial pressure of 50 psia. CO₂ desorption was measured at a temperature of 120°C and a partial pressure of 65 psia.

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Table 1 – CO₂ absorption and desorption

Amine	wt. % amine in absorbing fluid	CO ₂ Absorption Cycle (moles/litre)	CO ₂ Desorption Cycle (moles/litre)	Net CO ₂ absorption (moles/litre of absorbing fluid)
PMDETA	30	3.3	0.6	2.7
	50	4.2	0.8	4.2
	75	5.6	0.3	5.3
	90	2.4	0.2	2.2
	100	1.0	0.3	0.7
TMEDA	75	4.1	0.4	3.7
HMTETA	75	3.1	0.0	3.1
HMTETA	50	3.6	0.0	3.6
Blend 1*	90	4.4	0.0	4.4
Blend 2**	75	4.4	0.0	4.4
MDEA	50	3.8	0.4	3.4

*Blend 1 = 50% wt MDEA + 40% wt PMDETA + 10% wt water

5 **Blend 2 = 25% wt MDEA + 50% wt PMDETA + 25% wt water

It was found that the following absorbing fluids had a better net CO₂ absorption, based on equilibrium conditions, than the 50% by weight aqueous solution of N-methyldiethanolamine (MDEA):

- 10 75% by weight aqueous solution of pentamethyldiethylenetriamine (PMDETA), 75% by weight aqueous solution of tetramethylethylenediamine (TMEDA), 50% by weight

aqueous solution of PMDETA, 50% by weight aqueous solution of hexamethyltriethylenetetramine (HMTETA), Blend 1 and Blend 2.

Absorption of H₂S

The results presented in Table 2 were obtained using a gaseous stream comprising 12% by volume H₂S and 88% by volume methane. H₂S absorption was measured at a temperature of 40°C and a partial pressure of 50 psia. H₂S desorption was measured at a temperature of 120°C and a partial pressure of 65 psia.

Table 2 – H₂S absorption and desorption

Amine	wt. % amine in absorbing fluid	H ₂ S Absorption Cycle (moles/litre)	H ₂ S Desorption Cycle (moles/litre)	Net H ₂ S absorption (moles/litre of absorbing fluid)
PMDETA	30	2.8	0.7	2.1
	50	4.4	0.0	4.4
	75	6.2	0.4	5.8
	90	3.9	0.2	3.7
	100	2.0	0.3	1.7
TMEDA	75	2.8	0.4	2.4
Blend 1*	90	5.4	0.6	4.8
Blend 2**	75	4.9	0.0	4.9
MDEA	50	4.3	0.2	4.1

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*Blend 1 = 50% wt MDEA + 40% wt PMDETA + 10% wt water

**Blend 2 = 25% wt MDEA + 50% wt PMDETA + 25% wt water

It was found that the following absorbing fluids had a better net H₂S absorption, based on equilibrium conditions, than a 50% by weight aqueous solution of N-

methylidieanolamine (MDEA);
50% by weight aqueous solution of pentamethylidiethylenetriamine (PMDETA), 75%
by weight aqueous solution of PMDETA, Blend 1 and Blend 2.

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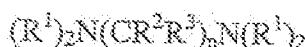
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Claims:

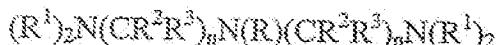
1. A process for the removal of an acid gas from a gaseous feed stream comprising:
 (A) an absorption step of bringing the gaseous feed stream into gas-liquid contact with
 an absorbing fluid, whereby at least a portion of the acid gas present in the gaseous
 stream is absorbed into the absorbing fluid to produce (a) a refined gaseous stream
 having a reduced acid gas content and (b) an acid gas rich absorbing fluid, wherein the
 absorbing fluid comprises an aqueous solution of at least one tertiary alkylamine
 wherein the concentration of tertiary alkylamine in the aqueous solution is above 60%
 by weight, preferably in the range 62.5 to 90% by weight, and the tertiary alkylamine is
 selected from the group consisting of:

10 diamines of formula I



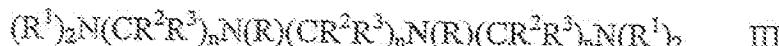
I

triamines of formula II



II

and tetramines of formula III



III

where each R is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably
 methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a

substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4; however, it is preferred that R² and R³ are each hydrogen and n is an integer from 2 to 4, preferably 2; and

5 (B) a regeneration step of heating the acid gas rich absorbing fluid at atmospheric pressure whereby a gaseous stream comprising the acid gas is liberated and an acid gas lean absorbing fluid is regenerated and recycled for use in the absorption step.

10 2. A process as claimed in Claim 1 wherein the concentration of tertiary alkylamine in the aqueous solution is in the range 70 to 80% by weight.

15 3. A process for the removal of an acid gas from a gaseous feed stream comprising:
 (A) an absorption step of bringing the gaseous feed stream into gas-liquid contact with an absorbing fluid, whereby at least a portion of the acid gas present in the gaseous stream is absorbed into the absorbing fluid to produce (a) a refined gaseous stream having a reduced acid gas content and (b) an acid gas rich absorbing fluid, wherein the absorbing fluid comprises an aqueous solution of at least one tertiary alkylamine selected from the group consisting of:

20 diamines of formula I

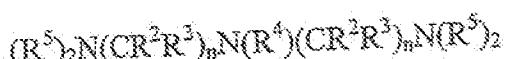


I

where each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably 25 methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4;

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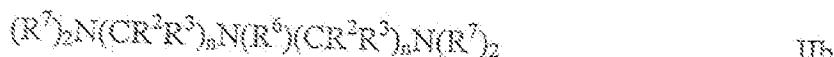
triamines of formula IIa



IIa

where R⁴ is a substituted or unsubstituted C₂ - C₄ alkyl, preferably ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R⁵ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R⁵ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4;

10 triamines of formula IIb



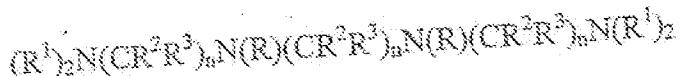
where R⁶ is a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R⁷ is independently a substituted or unsubstituted C₂ - C₄ alkyl selected from ethyl, n-propyl, i-propyl, n-butyl, i-butyl and t-butyl or, alternatively, the two R⁷ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4; and

triamines of formula IIc



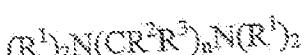
where R is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R⁸ and R⁹ are independently a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR⁸R⁹ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4;

and tetramines of formula III



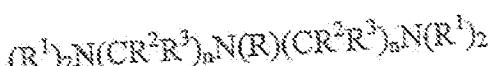
III

- where each R is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4; and
- (B) a regeneration step of heating the acid gas rich absorbing fluid at atmospheric pressure whereby a gaseous stream comprising the acid gas is liberated and an acid gas lean absorbing fluid is regenerated and recycled for use in the absorption step.
4. A process for the removal of an acid gas from a gaseous feed stream comprising:
- (A) an absorption step of bringing the gaseous feed stream into gas-liquid contact with an absorbing fluid, whereby at least a portion of the acid gas present in the gaseous stream is absorbed into the absorbing fluid to produce (a) a refined gaseous stream having a reduced acid gas content and (b) an acid gas rich absorbing fluid, wherein the absorbing fluid comprises an aqueous solution of at least one tertiary alkylamine selected from the group consisting of:
- 20 diamines of formula I



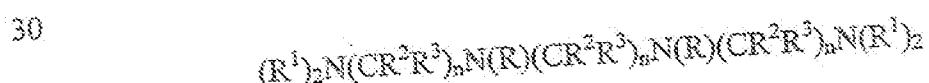
I

- 25 triamines of formula II



II

- and tetramines of formula III



III

where each R is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4; however, it is preferred that R² and R³ are each hydrogen and n is an integer from 2 to 4, preferably 2; and

10 (B) a regeneration step of heating the acid gas rich absorbing fluid at a pressure greater than atmospheric pressure whereby a gaseous stream comprising the acid gas is liberated and an acid gas lean absorbing fluid is regenerated and recycled for use in the absorption step.

5. A process as claimed in Claim 4 wherein the acid gas rich absorbing fluid is heated in the regeneration step at a pressure of at least 3 kg/cm² (absolute).

15. A process as claimed in Claim 5 wherein the acid gas rich absorbing fluid is heated in the regeneration step at a pressure of less than 10 kg/cm² (absolute).

6. A process as claimed in Claim 6 wherein the acid gas rich absorbing fluid is heated in the regeneration step at a pressure in the range 5 to 9.5 kg/cm² (absolute).

20 7. A process as claimed in any one of the preceding claims wherein the absorption step is carried out at a temperature of from 20 to 70°C.

8. A process as claimed in any one of the preceding claims wherein the acid gas rich absorbing fluid is heated in the regeneration step to a temperature of at least 100°C.

10. A process as claimed in any one of the preceding claims wherein the acid gas is selected from carbon dioxide and hydrogen sulphide.

25 11. A process as claimed in any one of the preceding claims wherein the gaseous feed stream is a high-pressure gaseous feed stream having a pressure of at least 15 kg/cm² (absolute) and an acid gas content of at least 1% by volume.

12. A process as claimed in any one of claims 1 to 10 wherein the gaseous feed stream is a low-pressure gaseous feed stream having a pressure of less than 3 kg/cm² (absolute) and an acid gas content of at least 1.5 % by volume.

13. A process as claimed in Claim 11 wherein the amount of carbon dioxide in the refined gaseous stream is less than 2 % by volume.

14. A process as claimed in Claims 11 or 12 wherein the amount of carbon dioxide in the refined gaseous stream is 50 ppmv or less.

15. A process as claimed in any one of Claims 11 to 14 wherein the amount of hydrogen sulphide in the gaseous feed stream is at least 0.02% by volume.

5 16. A process as claimed in Claim 15 wherein the amount of hydrogen sulphide in the refined gaseous stream is 10 ppmv or less.

10 17. A process as claimed in any one of the preceding claims wherein the number of moles of basic groups per litre of aqueous amine solution (B) is at least 4, preferably at least 6 where $B = [1000 \times (\text{aqueous amine solution density}) \times (\text{weight fraction of tertiary alkylamine}) \times (\text{number of basic groups per molecule of tertiary alkylamine})]/\text{molecular weight of tertiary alkylamine}$.

18. A process as claimed in any one of the preceding claims wherein the gaseous stream liberated in the regeneration step is dumped into an underground zone.

19. A process as claimed in any one of the preceding claims wherein the absorbing fluid is an aqueous solution of at least one tertiary alkylamine selected from the group consisting of tetramethylethylenediamine, tetraethylethylenediamine, tetramethyl-1,3-propanediamine, tetraethyl-1,3-propanediamine, tetramethyl-1,3-butanediamine, tetramethyl-1,4-butanediamine, tetraethyl-1,3-butanediamine, tetraethyl-1,4-butanediamine, pentamethyldiethylenetriamine, pentaethylidiethylenetriamine, pentamethyldipropylenetriamine, pentamethyl-(2-aminoethyl)-1,3-propanetriamine, hexamethyltriethylenetetramine and hexaethyltriethylenetetramine.

20 20. A process as claimed in any one of the claims 4 to 19 wherein the concentration of tertiary alkylamine in the aqueous solution is above 60% by weight, preferably in the range 62.5 to 90% by weight, most preferably in the range 70 to 80% by weight.

25 21. A process as claimed in any one of the preceding claims wherein the aqueous solution further comprises an absorption promoter.

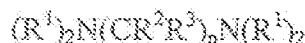
22. A process as claimed in any one of the preceding claims wherein the aqueous solution comprises a further absorbent selected from the group consisting of N-methyldiethanolamine (MDEA), triethanolamine, and potassium carbonate.

30 23. A process as claimed in Claim 22 wherein the concentration of the further absorbent in the aqueous solution is in the range 1 to 40% by weight.

24. An absorbing fluid composition for removing an acid gas from a gaseous feed stream, the composition comprising at least one tertiary alkylamine selected from the

group consisting of:

diamines of formula I



I

5

triamines of formula II



II

10 and tetramines of formula III



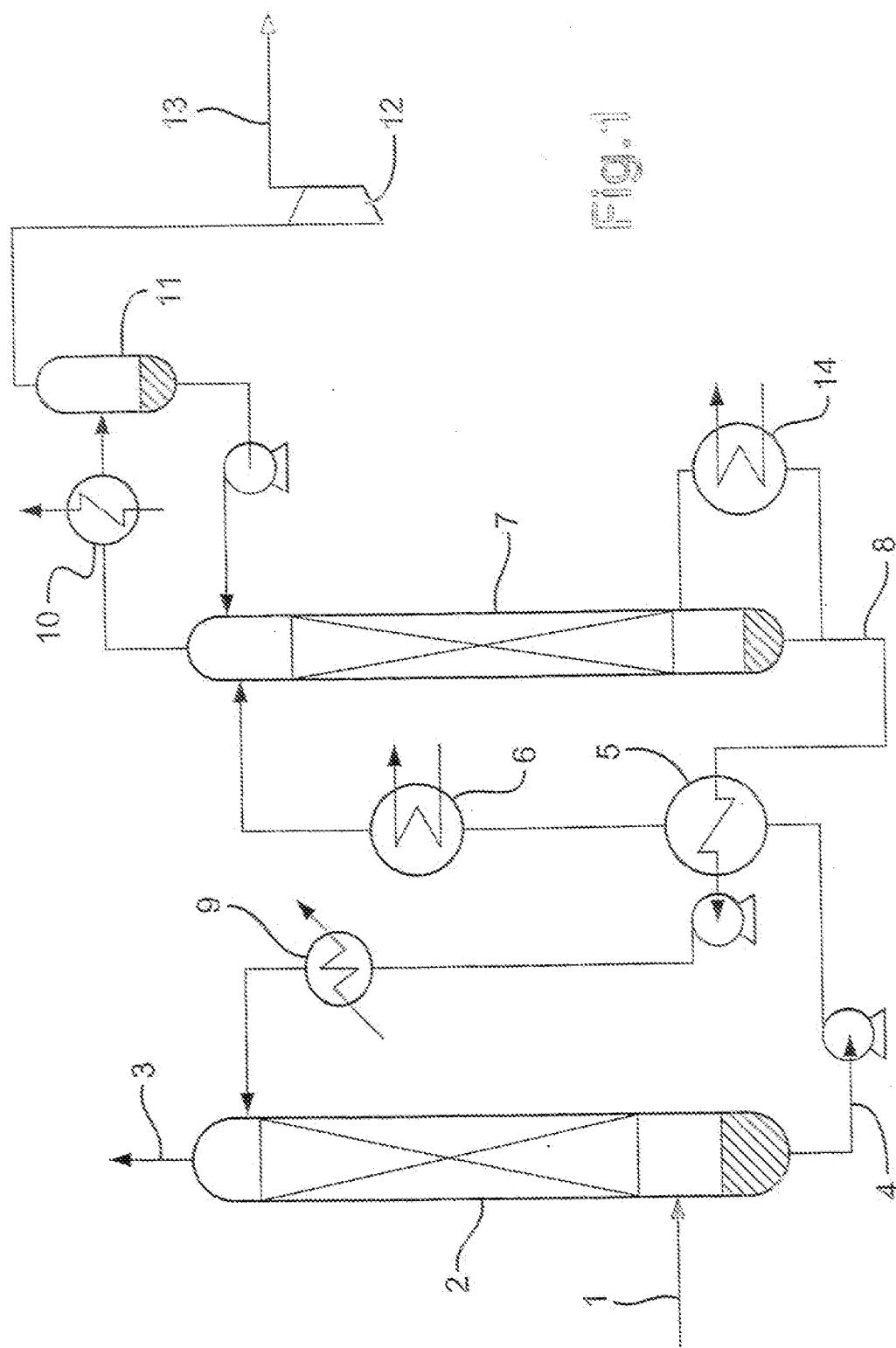
III

where each R is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably 15 methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl; each R¹ is independently a substituted or unsubstituted C₁ - C₄ alkyl, preferably methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or t-butyl or, alternatively, the two R¹ groups together with the nitrogen atom form a heterocyclic ring, for example a pyrrole ring; R² and R³ are independently a hydrogen or a C₁ - C₄ alkyl group, preferably methyl or ethyl, and each of the CR²R³ 20 groups are the same or different and n is an integer from 1 to 4, preferably 2 to 4; however, it is preferred that R² and R³ are each hydrogen and n is an integer from 2 to 4, preferably 2 as an aqueous solution of greater than 60% by weight tertiary alkylamine, preferably, 62.5 to 90% by weight, more preferably 70 to 80% by weight.

25. An absorbing fluid composition as claimed in Claim 24 wherein the aqueous 25 solution further comprises an absorption promoter.

26. An absorbing fluid composition as claimed in Claims 24 or 25 wherein the aqueous solution comprises a further absorbent selected from the group consisting of N-methyldiethanolamine (MDEA), triethanolamine, and potassium carbonate.

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INTERNATIONAL SEARCH REPORT

PCT/GB2004/000791

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 801D53/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 801D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 267 939 B1 (NAGY ZOLTAN ET AL) 31 July 2001 (2001-07-31) cited in the application column 1, line 57 - column 4, line 28	1,24

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

13 July 2004

Date of mailing of the international search report

22/07/2004

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INTERNATIONAL SEARCH REPORT
Information on patent family members

PCT/GB2004/000791

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
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